## MS.40.4

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### Perovskites $ABX_3$ under pressure: Transition to post-perovskite $CaIrO_3$ type and other scenarios

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Recently we have performed a systematic quantitative analysis of crystal structure distortion for ~1300 $ABX_3$ perovskites in terms of A- to B-site polyhedra volume ratios VA/VB [1]. The analysis identified a number of compositions close to the boundary of perovskite type stability which we have studied experimentally by in situ high-pressure synchrotron X-ray powder diffraction. Here we will present the results of these experiments for several materials studied under pressure for the first time and will discuss our theoretical and experimental findings focusing on the following aspects of perovskite (pv) and post-perovskite $CaIrO_3$ (ppv) structure types: (1) interplay between geometry and symmetry in distorted perovskites (is there any intermediate phase between pv and ppv?); (2) topological and geometrical constraints for $ABX_3$ stoichiometry (what might be the structure of hypothetical structure types denser than ppv?); and (3) the effect of vacancies in $ABX_3$ and pressure-induced amorphization as an alternative to pv-ppv transition.
[1] M. Avdeev, E. Caspi, S. Yakovlev, Acta Cryst B 63 (2007) 363.

Keywords: perovskites, phase transitions and structure, amorphization under pressure

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### *Ab-initio* crystallography of kaolin minerals: Synthesis, diagenesis and mantle pressures

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In this abundantly illustrated talk, we deduce ab initio the stable kaolin phases and explain nearly all observations about the kaolin system, starting from just ideal topology of kaolin layers $Al_2Si_2O_5(OH)_4$ and basic scheme for interlayer H bonds [Acta Cryst. B64 (2008)]. Energy independence of non-neighbour layers leads to a complete list of 36 possible lowest-energy polytype models. VASP optimization of ideal cells and coordinates gives total energies. The four known kaolin minerals, including experimental distortions, are among the 36 optimized models created from ideal geometry. Using ab initio energies and cell volumes, we build a 0K enthalpy/pressure graph. We read off this graph that kaolinite and dickite are lowest-energy solutions, whereas nacrite and HP-dickite are lowest-enthalpy solutions at moderate pressure (P). Minor temperature (T) dependence of this novel calculated 0K graph would explain current facts about synthesis and diagenesis of kaolin minerals. Kaolinite is the stable phase at ambient T and P<1GPa. HP-dickite is the stable phase that forms at P>2GPa for T>300K but transforms reversibly to dickite at ambient conditions. Nacrite forms over a narrow stability domain wedged between kaolinite and HP-dickite at T-P combinations not found with normal geothermal gradients. Mineralogical reports about mutual transformation of kaolinite, dickite and nacrite all involve dissolution and recrystallization, a necessity for polytypes with different layer-to-layer rotations. Ab initio compression to 60GPa of 19 polytype models involving no layer-to-layer rotations shows that kaolinite survives up to ~12GPa. Beyond that pressure, novel kaolin polytypes with different H-bonding not possible at ambient conditions become prime candidates for post-kaolinite phases.

Keywords: *ab-initio* calculations, polytypism, mineralogy and crystallography

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### Solving zeolite structures using electron crystallography

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Zeolite structures can be very challenging to solve, particularly in early stages of synthesis and characterisation when the samples are poorly crystallised. The crystallite sizes are often so small that peak broadening makes the powder patterns hard to deconvolute, and often they become nm sized so that only electron diffraction can be used to solve them, and this technique presents its own challenge with problems associated with dynamical scattering, sample bending, multiple scattering, the missing cone problem etc. Recently we have applied techniques that use density building functions and density histogram matching methods coupled with entropy maximisation and likelihood analysis to solve a number of structures ab initio using both electron diffraction data in 2- and 3-dimensions most of which were collected using the precession method.
1. A low resolution structure is generated using low resolution structure factors combined with the origin defining rules of direct methods [2].
2. New reflections are given permuted phase angles and analysed using density building functions [3] or density building functions are used to improve the resolution of the low resolution maps.
3. Phase sets are selected according to density criteria and subjected to entropy maximisation [4].
4. Likelihood and density histograms are used to select the optimal phase set from these.
The method is quick,and largely automatic.
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4. Bricogne, G & Gilmore, C.J. (1990). Acta Cryst. A46, 284-297.

Keywords: electron crystallography, zeolites, precession method

## MS.41.2

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### Prospects for structure solution by electron diffraction of three-dimensional protein crystals

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